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(54) Laundry and cleaning compositions

(57) The present invention relates to a laundry and cleaning composition comprising a detergent ingredient and a product of reaction between an amino functional polymer comprising at least one primary amine group, and a perfume component. By the present invention, there is obtained a release of the active component over a longer period of time than by the use of the active itself.

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**Description**Field of the invention

**[0001]** The present invention relates to laundry and cleaning compositions comprising a product of reaction between an amino functional polymer comprising at least one primary amine group, and a perfume component, in particular aldehyde or ketone perfumes.

Background of the invention

**[0002]** Laundry and cleaning products are well-known in the art. However, consumer acceptance of laundry and cleaning products is determined not only by the performance achieved with these products but also by the aesthetics associated therewith. The perfume components are therefore an important aspect of the successful formulation of such commercial products.

**[0003]** It is also desired by consumers for laundered fabrics to maintain the pleasing fragrance over time. Indeed, perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carried-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Furthermore, fragrance materials are often very costly and their inefficient use in laundry and cleaning compositions and ineffective delivery to fabrics results in a very high cost to both consumers and laundry and cleaning manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in laundry and cleaning products, especially for improvement in the provision of long-lasting fragrance to the fabrics.

**[0004]** One solution is to use carrier mechanisms for perfume delivery, such as by encapsulation. This is taught in the prior art and described in U.S. 5,188,753.

**[0005]** Still another solution is to formulate compounds which provide a delayed release of the perfume over a longer period of time than by the use of the perfume itself. Disclosure of such compounds may be found in WO 95/04809, WO 95/08976 and co-pending application EP 95303762.9.

**[0006]** However, notwithstanding the advances in the art, there is still a need for a compound which provides a delayed release of the perfume component.

**[0007]** That need is even more acute for perfume ingredients which are characteristic of the fresh notes, namely the aldehydes and ketones perfume ingredients. Indeed, whilst these provide a fresh fragrance, these perfumes are also very volatile and have a low substantivity on the surface to be treated like fabrics.

**[0008]** Accordingly, it is a further object of the invention to provide a laundry and cleaning composition comprising a perfume component which provides a fresh fragrance and is substantive to the treated surface.

**[0009]** The Applicant has now found that specific reaction products of an amino functional polymer comprising at least one primary amine group with an active aldehyde or ketone, such as imines compounds, also provide a delayed release of the active such as a perfume.

**[0010]** Imine compounds are known in the art under the name of Schiff bases which is the condensation of an aldehyde perfume ingredient with an anthranilate. A typical description can be found in US 4853369. By means of this compound, the aldehyde perfume is made substantive to the fabrics. However, a problem encountered with these schiff bases is that the methylantranilate compound also exhibits a strong scent, which as a result produces a mixture of fragrances, thereby reducing or even inhibiting the aldehyde fragrance perception.

**[0011]** To achieve such perfume composition with comparable aldehyde or ketones fresh notes whilst still having satisfactory fabric substantivity, perfumers have formulated around the composition. For example, by having a carrier or encapsulating material for such notes such as with cyclodextrin, zeolites or starch.

**[0012]** Still another solution is the use of a glucosamine as described in JP 09040687. However, this compound has been found to give a very low stability in the wash/cleaning process. As a result, insufficient perfume residuality on the treated fabric and/or hard surface has been found with these glucosamine compounds.

**[0013]** A further solution is described in Chemical release control, Kamogawa et Al., J. Poly. Sci. Polym. Chem. Ed. Vol 20, 3121 (1982) which describe the use of amino styrene compounds condensed with aldehydes perfumes, whereby the release of the perfume is triggered by means of copolymerisation or acidification of the compound. Its use in laundry and cleaning product is however not mentioned.

**[0014]** The Applicant has now found that a reaction product of an amino functional polymer comprising at least one primary amine group, and a perfume component also fulfill such a need.

**[0015]** Another advantage of the compounds of the invention is their ease of manufacture rendering their use most desirable.

Summary of the invention

**[0016]** The present invention relates to a laundry and cleaning composition comprising a detergent ingredient and a product of reaction between an amino functional polymer comprising at least one primary amine group and a perfume component selected from ketone, aldehyde, and mixtures thereof, characterised in that said amino functional polymer has an Odour Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol, and the product of reaction a Dry Surface Odour Index of more than 5.

[0017] In a further aspect of the invention, there is provided a method of delivering residual fragrance to a surface by means of the compound or composition of the invention.

#### Detailed description of the invention

#### **I-Product of reaction between an amino functional polymer and a perfume component**

[0018] An essential component of the invention is a product of reaction an amino functional polymer comprising at least one primary amine group and a perfume component, so called hereinafter "amine reaction product".

#### **A- Amino functional polymer**

[0019] The amino functional polymer is characterized by an Odour Intensity Index of less than that of a 1 % solution of methylantranilate in dipropylene glycol.

#### **Odour Intensity Index method**

[0020] By Odour Intensity Index, it meant that the pure chemicals were diluted at 1% in Dipropylene Glycol, odor-free solvent used in perfumery. This percentage is more representative of usage levels. Smelling strips, or so called "blotters", were dipped and presented to the expert panellist for evaluation. Expert panellists are assessors trained for at least six months in odor grading and whose gradings are checked for accuracy and reproducibility versus a reference on an ongoing basis. For each an amino functional polymer, the panellist was presented two blotters: one reference (Me Anthranilate, unknown from the panellist) and the sample. The panellist was asked to rank both smelling strips on the 0-5 odor intensity scale, 0 being no odor detected, 5 being very strong odor present.

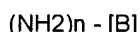
#### **Results:**

[0021] The following represents Odour Intensity Index of an amino functional polymer suitable for use in the present invention and according to the above procedure.

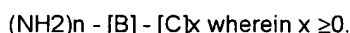
[0022] In each case, numbers are arithmetic averages among 5 expert panellists and the results are statistically significantly different at 95% confidence level:

Methylantranilate 1% (reference)	3.4
1,4-bis-(3-aminopropyl)piperazine (BNPP) 1%	1.0

[0023] A general structure for the amino functional polymer containing at least one primary amine group of the present invention, is as follows:



wherein n is an index of at least 1 and B is the polymer backbone. B can optionally comprise a branching group, C and hence the amino functional polymer is of the following formula:

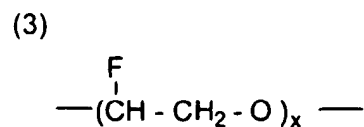
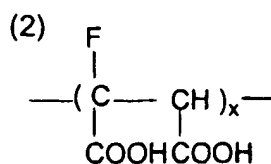
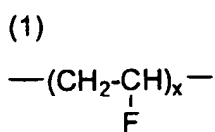


[0024] The amino functional polymer of the present invention contains at least one free, unmodified primary amino group attached to the main chain by hydrogen substitution, or by other suitable insertion or substitution by groups referred to as R\*. Also suitable is the amino functional polymer comprising an unmodified primary amino group present on side chain(s).

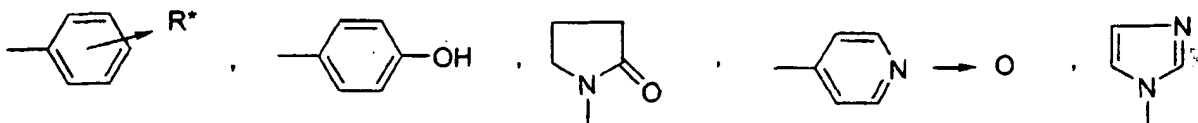
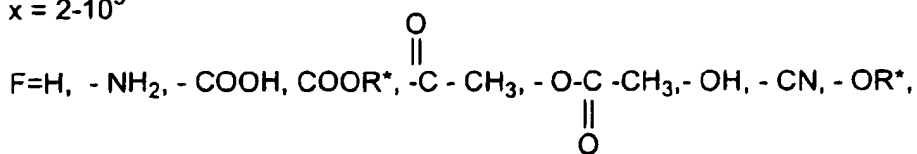
[0025] Preferably, the amino functional polymers of the present invention will comprise several amino groups, more preferably more than 10 amino groups. The amino functional polymers of the present invention will preferably present a molecular weight (MW) ranging from 150 to 2.10E6; more preferably from 400-50,000; most preferably from 600 to 40,000.

[0026] The amino functional polymer can be a linear homo-, co-polymer and optionally branched, grafted and/or cross-linked.

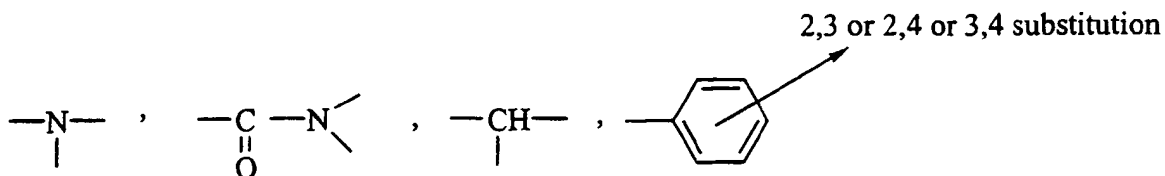
[0027] Suitable polymer backbone B for the purpose of the present invention have the following polymer units :



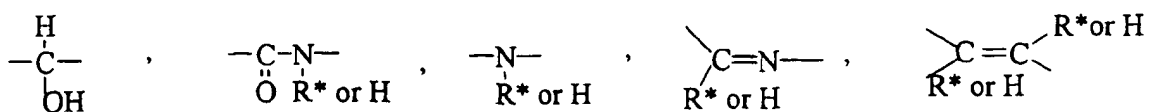
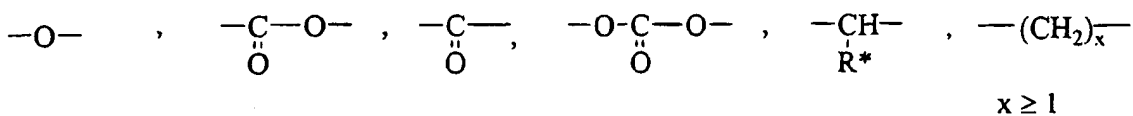
wherein  $x = 2-10^5$

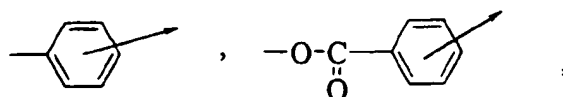
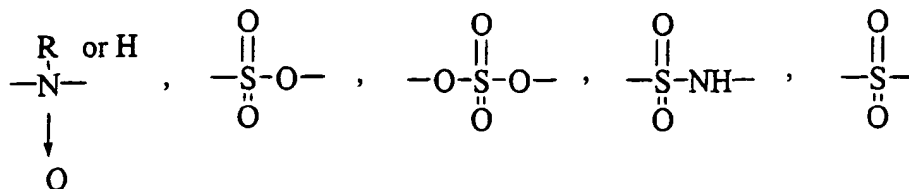


[0028] Suitable branching units C for the polymer backbone B are :

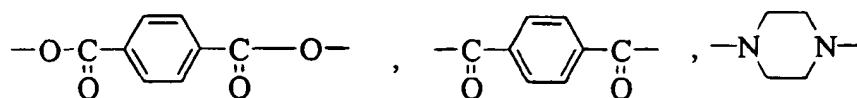


[0029] The polymer backbone B can also comprise insertion groups I such as :

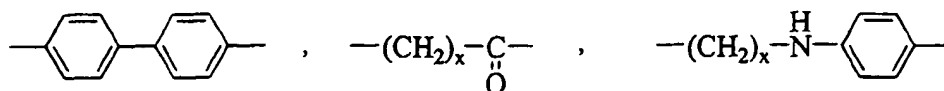




[0030] The arrow indicates substitution in position 2,3 or 4



[0031] The backbone (B) can also contain several insertion groups linked together: e.g.

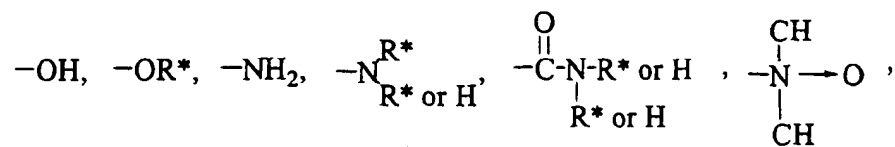


wherein  $x \geq 1$ .

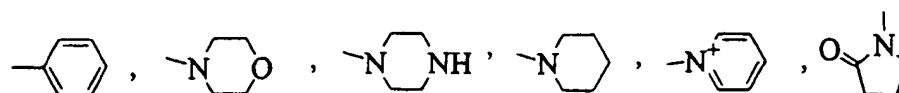
[0032] The aminofunctional polymers of the present invention can further comprise substituents  $R^*$  in the main chain or in the side chain(s). Typically,  $R^*$  replaces an hydrogen atom. This  $R^*$  group can either be linked directly or via a linker group L to the main or side chain. Suitable linker groups L are the above mentioned insertion groups I.

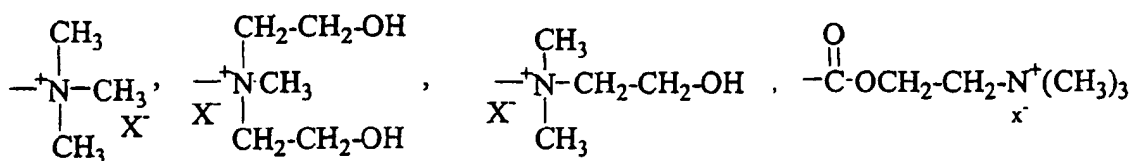
[0033]  $R^*$  groups are C1 to C22 alkyl, alkenyl, alkylbenzene chain and/or their corresponding substituted derivatives. Such corresponding substituted derivatives include alicyclic, aromatic, heteroaromatic or heterocyclic systems, either inserted in the main chain or incorporated by a substitution of an H atom in the main chain; an insertion group I in the main chain, as defined herein above and/or an end group E as defined below.

[0034] Further, the polymer backbone B and  $R^*$  encompass end groups E. Typically end groups E can be an H,  $\text{NH}_2$  groups, an aromatic, alicyclic, heteroaromatic or heterocyclic group including mono-, di-, oligo-, poly-saccharides :



$\text{---SO}_3\text{H}, \text{---OSO}_3\text{H}, \text{---COOH}, \text{---COOR}^*,$





wherein  $\text{X}^-$  is an anion like  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SO}_4^{2-}$ .

[0035] In addition, the  $\text{R}^*$  group can also be modified via substitution of one or more H atoms. Said substitution can either be an end group E or an insertion group I as defined above, where the insertion group is terminated by a H, E or  $\text{R}^*$  group.

[0036] Examples of suitable amino functional polymers containing at least one primary amine group for the purpose of the present invention are :

- Polyvinylamine with a MW of about 300-2.10E6;
- Polyvinylamine alkoxyated with a MW of about 600, 1200 or 3000 and an ethoxylation degree of 0.5;
- Polyvinylamine vinylalcohol - molar ratio 2:1, polyvinylaminevinylformamide - molar ratio 1:2 and polyvinylamine vinylformamide-molar ratio 2:1;
- Triethylenetetramine, diethylenetriamine, tetraethylenepentamine;
- Bis-aminopropylpiperazine;
- Polyamino acid (L-lysine / lauric acid in a molar ratio of 10/1), Polyamino acid (L-lysine / aminocaproic acid / adipic acid in a molar ratio of 5/5/1), Polyamino acid (L-lysine / aminocaproic acid / ethylhexanoic acid in a molar ratio of 5/3/1) Polyamino acid (polylysine-cocaprolactam);
- amino substituted polyvinylalcohol with a MW ranging from 400-300,000;
- polyoxyethylene bis [amine] available from e.g. Sigma;
- polyoxyethylene bis [6-aminohexyl] available from e.g. Sigma;
- N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched (TPTA); and
- 1,4-bis-(3-aminopropyl) piperazine (BNPP).

[0037] Preferred amino functional polymers containing at least one primary amine group are :

- polyvinylamines with a MW ranging from 600, 1200, 3K, 20K, 25K or 50K;
- amino substituted polyvinylalcohol with a MW ranging from 400-300,000;
- polyoxyethylene bis [amine] available from e.g. Sigma;
- polyoxyethylene bis [6-aminohexyl] available from e.g. Sigma;
- N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched (TPTA)
- 1,4-bis-(3-aminopropyl) piperazine (BNPP).

[0038] Furthermore, such amino functional polymers comprising at least one primary amine group and the amine reaction product provide fabric appearance benefits, in particular color care and protection against fabric wear.

The appearance of fabrics, e.g., clothing, bedding, household fabrics like table linens is one of the area of concern to consumers. Indeed, upon typical consumer's uses of the fabrics such as wearing, washing, rinsing and/or tumble-drying of fabrics, a loss in the fabric appearance; which can be at least partly due to loss of color fidelity and color definition, is observed. Such a problem of color loss is even more acute after multiwash cycles. It has been found that the compositions of the present invention provide improved fabric appearance and protection against fabric wear and improved color care to laundered fabrics, especially after multiwash cycles.

[0039] Therefore, the softening compositions of the present invention can provide simultaneously fabric care and

long lasting perfume benefits.

## B-Perfum

**[0040]** Preferably, for the above mentioned compounds, by perfume ketone or aldehyde, it is meant any chain containing at least 1 carbon atom, preferably at least 5 carbon atoms.

**[0041]** A typical disclosure of suitable ketone and/or aldehydes, traditionally used in perfumery, can be found in "perfume and Flavor Chemicals", Vol. I and II, S. Arctander, Allured Publishing, 1994, ISBN 0-931710-35-5.

**[0042]** Perfume ketones components include components having odoriferous properties.

**[0043]** Preferably, for the above mentioned compounds, the perfume ketone is selected for its odor character from buccoxime; iso jasmone; methyl beta naphthyl ketone; musk indanone; tonalid/musk plus; Alpha-Damascone, Beta-Damascone, Delta-Damascone, Iso-Damascone, Damascenone, Damarose, Methyl-Dihydrojasmonate, Menthone, Carvone, Camphor, Fenchone, Alpha-Ionone, Beta-Ionone, Gamma-Methyl so-called Ionone, Fleuramone, Dihydrojasmonone, Cis-Jasmonone, Iso-E-Super, Methyl- Cedrenyl-ketone or Methyl- Cedrylone, Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-Butanone, Celery Ketone or Livescone, 6-Isopropyldecahydro-2-naphtone, Dimethyl-Octenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3,5,5-tetramethyl-Cyclohexanone, Methyl-Heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p-Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3-methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl-Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)-Indanone, 4-Damascol, Dulcinyll or Cassione, Gelsone, Hexalon, Isocyclemone E, Methyl Cyclocitronone, Methyl-Lavender-Ketone, Orivon, Para-tertiary-Butyl-Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plicatone, Veloutone, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Tetrameran, Undecalactone and Gamma undecalactone.

**[0044]** For the above mentioned compounds, the more preferred ketones are selected for its odor character from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.

**[0045]** Perfume aldehyde components include components having odoriferous properties.

**[0046]** Preferably, for the above mentioned compounds, the perfume aldehyde is selected for its odor character from adoxal; anisic aldehyde; cymal; ethyl vanillin; florhydal; helional; heliotropin; hydroxycitronellal; koavone; lauric aldehyde; lyral; methyl nonyl acetaldehyde; P. T. buccinal; phenyl acetaldehyde; undecylenic aldehyde; vanillin; 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amyll cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl) propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al, [(3,7-dimethyl-6-octenyl)oxy] acetaldehyde, 4-isopropylbenzaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)]-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha, alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5,9-undecadienal, 2-methyl-3-(4-tertbutyl)propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carboxaldehyde, 5 or 6 methoxyhexahydro-4,7-methanoindan-1-or 2-carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclohexenecarboxaldehyde, 7-hydroxy-3,7-dimethyl-octanal, trans-4-decenal, 2,6-nonadial, paratolylacetaldehyde; 4-methylphenylacetaldehyde, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylen-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyl octanal, alpha-methyl-4-(1-methyl ethyl) benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para methyl phenoxy acetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethyl hexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1]-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, 1-p-menthene-q-carboxaldehyde and mixtures thereof.

**[0047]** More preferred aldehydes are selected for its odor character from 1-decanal, benzaldehyde, florhydal, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadial; alpha-n-amyll cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Buccinal, lyral, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof.

**[0048]** In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

**[0049]** In another embodiment, especially suitable for the purpose of the present invention are the perfume compounds, preferably the perfume ketones or aldehydes, characterized by having a low Odor Detection Threshold. Such Odor Detection Threshold (ODT) should be lower than 1ppm, preferably lower than 10ppb - measured at controlled Gas Chromatography (GC) conditions such as described here below. This parameter refers to the value commonly used in the perfumery arts and which is the lowest concentration at which significant detection takes place



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that some odorous material is present. Please refer for example in "Compilation of Odor and Taste Threshold Value Data (ASTM DS 48 A)", edited by F. A. Fazzalari, International Business Machines, Hopwell Junction, NY and in Calkin et al., Perfumery, Practice and Principles, John Wiley & Sons, Inc., page 243 et seq (1994). For the purpose of the present invention, the Odor Detection Threshold is measured according to the following method :

The gas chromatograph is characterized to determine the exact volume of material injected by the syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.02 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine the ODT of a perfume material, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average over all panelists determines the threshold of noticeability. The necessary amount of analyte is injected onto the column to achieve a certain concentration, such as 10 ppb, at the detector. Typical gas chromatograph parameters for determining odor detection thresholds are listed below.

GC: 5890 Series II with FID detector

7673 Autosampler

Column: J&W Scientific DB-1

Length 30 meters ID 0.25 mm film thickness 1 micron

Method:

Split Injection: 17/1 split ratio

Autosampler: 1.13 microliters per injection

Column Flow: 1.10 mL/minute

Air Flow: 345 mL/minute

Inlet Temp. 245°C

Detector Temp. 285°C

Temperature Information

Initial Temperature: 50°C

Rate: 5C/minute

Final Temperature: 280°C

Final Time: 6 minutes

Leading assumptions: 0.02 minutes per sniff

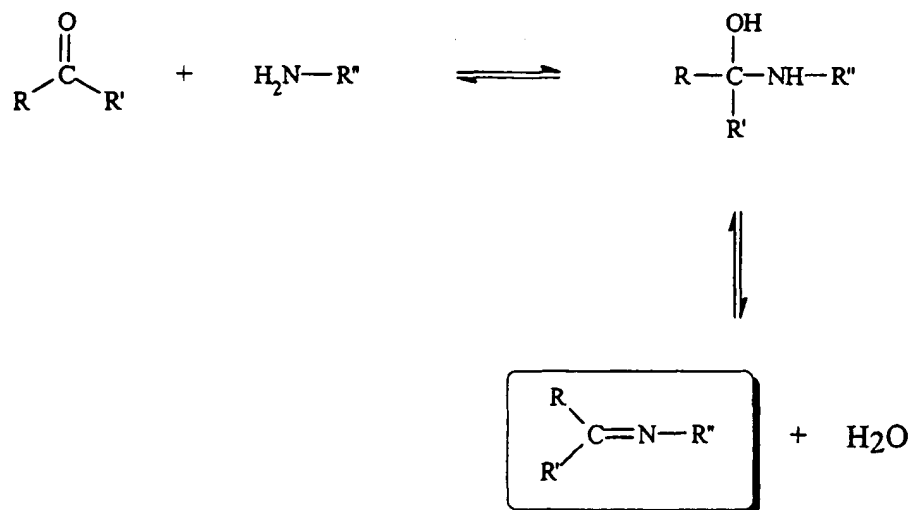
GC air adds to sample dilution

**[0050]** Examples of such preferred perfume components are those selected from : 2-methyl-2-(para-isopropylphenyl)-propionaldehyde, 1-(2,6,6-trimethyl-2-cyclohexan-1-yl)-2-buten-1-one and/or para-methoxyacetophenone. Even more preferred are the following compounds having an ODT  $\leq 10$ ppb measured with the method described above : undecylenic aldehyde, undecalactone gamma, heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxyphenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methyl-nonyl ketone:

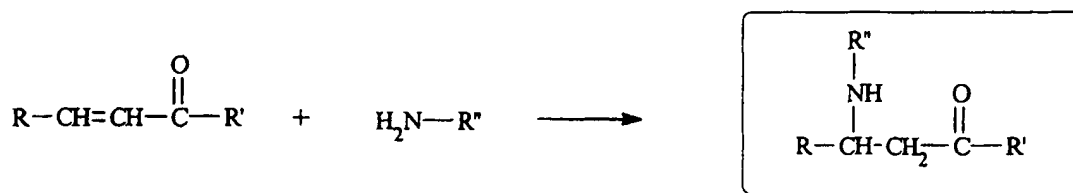
### Process

**[0051]** Preparation of the component is made as follows in the Synthesis Examples. In general, the nitrogen analogs of ketones and aldehydes are called azomethines, Schiff bases or the more preferred name imines. These imines can easily be prepared by condensation of primary amines and carbonyl compounds by elimination of water.

**[0052]** A typical reaction profile is as follows:



$\alpha,\beta$ -Unsaturated ketones do not only condense with amines to form imines, but can also undergo a competitive 1,4-addition to form  $\beta$ -aminoketones.



[0053] By means of this simple method, compound and composition containing said compounds are made which achieve a delayed release of the active ingredient.

[0054] As can be observed, the perfume ingredient needs to be present in equimolar amount to the amine function so as to enable the reaction to take place and provide the resulting amine reaction product. Of course, higher amounts are not excluded and even preferred when the amine compound comprises more than one amine function.

#### Mechanism of release

[0055] By the present invention, a delayed release of a perfume ingredient, i.e. ketone or aldehyde is obtained. Not to be bound by theory, the release is believed to occur by the following mechanisms:

[0056] For imine compounds, the perfume components are released upon breaking down of the imine bond, leading to the release of the perfume component and of the primary amine compound. This can be achieved by either hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

[0057] For  $\beta$ -aminoketone compounds, treatment with air moisture and/or water successfully releases the perfume component and the primary amine compound. However, other means of release are not excluded like hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

[0058] Still other means of release for imine as well as  $\beta$ -aminoketone compounds can be considered such as by the steaming step of ironing the treated fabric, tumble-drying, and/or wearing.

#### Laundry and cleaning compositions

[0059] The present invention includes both laundry and cleaning compositions which are typically used for laundering fabrics and cleaning hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of perfume ketone and/or aldehyde. Accordingly, by laundry and cleaning compositions, these are to be understood to include not only detergent compositions which provide fabric cleaning benefits, but also compositions such as hard surface cleaning which provide hard surface cleaning benefit.

[0060] Preferred are those laundry compositions which result in contacting the compound of the invention with fabric.

[0061] Preferably, the amine reaction product(s) which is incorporated into such laundry and cleaning compositions provides a dry surface Odour Index of more than 5 preferably at least 10.

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[0062] By Dry Surface Odour Index, it is meant that the amine reaction product(s) provides a Delta of more than 5, wherein Delta is the difference between the Odour Index of the dry surface treated with amine reaction product(s) and the Odour Index of the dry surface treated with only the perfume raw material.

### Measurement method of Dry Surface Odour Index:

[0063] For the above Dry Surface Odour Index, the amine reaction product suitable for use in the present invention needs to fulfill at least one of the following two tests. Preferred amine reaction product suitable for use in the present invention fulfill both test.

#### 1)-For fabric surface

##### Product preparation:

[0064] The amine reaction product is added to the unperfumed product base. Levels of amine reaction product are selected so as to obtain an odour grade on the dry fabric of at least 20. After careful mixing, by shaking the container in case of a liquid, with a spatula in case of a powder, the product is allowed to sit for 24 hrs.

##### Washing process:

[0065] The resulting product is added into the washing machine in the dosage and in the dispenser appropriate for its category. The quantity corresponds to recommended dosages made for the corresponding market products: typically between 70 and 150 g for a detergent powder or liquid via current dosing device like granulette, or ariellette. The load is composed of four bath towels (170g) using a Miele W830 washing machine at 40°C short cycle, water input: 15°Hardness at a temperature of 10-18°C, and full spin of 1200rpm.

[0066] The same process is applied for the corresponding free perfume ingredient in consideration and is used as the reference. Dosages, fabric loads and washing cycles for the reference and the sample are identical.

##### Drying Process:

[0067] Within two hours after the end of the washing cycle, spinned but still wet fabrics are assessed for their odors using the scale mentioned below. Afterwards, half of the fabric pieces are hung on a line for 24 hr drying, away from any possible contaminations. Unless specified, this drying takes place indoor. Ambient conditions are at temperature between 18-25°C and air moisture between 50-80%. The other half is placed in a tumble drier and undergoes a full "very dry" cycle, i.e. in a Miele, Novotronic T430 set on program white-extra dry (full cycle). Tumble dry fabrics are also assessed on the next day. Fabrics are then stored in opened aluminum bags in an odor free room, and assessed again after 7 days.

##### Odor Evaluations:

[0068] Odor is assessed by expert panellist smelling the fabrics. A 0-100 scale is used for all fabric odor gradings. The grading scale is as follows :

100 = extremely strong perfume odor

75 = very strong perfume odor

50 = strong odor

40 = moderate perfume odor

30 = slight perfume odor

20 = weak perfume odor

10 = very weak perfume odor

0 = no odor

[0069] A difference of more than 5 grades after one day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after one day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between the amine reaction product and the perfume raw material, after either 1 day or 7 days or both 1 day and 7 days, it can be concluded that the amine reaction product is suitable for use in the present invention, provided that the amine compound fulfill the Odour Intensity Index.

**2)-For hard surfac :****Product preparation:**

**[0070]** The perfume raw material or blend thereof is added and carefully mixed at 0.255% in the unperfumed Hard Surface Cleaner base. After mixing and standing for 24 hrs, the homogeneity of the product is checked. In case of phase separation due to poor solubility of the perfume ingredient(s) an appropriate amount of Sodium p. Cymene Sulfonate or another solubilising agent is added till a homogeneous solution is obtained.

**Cleaning process:**

**[0071]** Five grams of this solution are evenly applied on the upper side of a ceramic tile (875 square cm, e.g. from Vileroy-Boch). After 1 minute the tile is rinsed with 1 liter of tap water. The tile is then placed in a vertical position for 3 minutes to allow the rinse water to drip off.

**[0072]** Finally, the tile is placed in a clean and aerated perspex box (38 x 40 x 32 cm) with a removable cover that has a sliding-lid (10 x 10 cm) to allow expert evaluators to smell the interior phase of the box.

The odor in the box is evaluated just after placing the tile in it (fresh reading) and after 1, 2 and 6 hours.

**Odor Evaluation:**

**[0073]** The grading scale is as follows :

50 = very strong odor

40 = strong odor

30 = moderate odor

20 = slight odor

10 = weak odor

0 = no odor

**[0074]** Every test includes a blanc (unperfumed Hard Surface Cleaner) and in the case of testing perfume precursor, so-called amine reaction product the corresponding free perfume ingredient is also included so that the effect of the carrier is adequately measured.

**[0075]** Again as for the Dry surface Odour Index method for fabrics, a difference of more than 5 grades after 1 day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after 1 day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between the amine reaction product and the perfume raw material, after either 1 day or 7 day or both 1 day and 7 days, it can be concluded that the amine reaction product is suitable for use in the present, provided that the amine compound fulfill the Odour Intensity Index.

**[0076]** The amine reaction product as defined herein before is typically comprised from 0.0001% to 10%, preferably from 0.001% to 5%, and more preferably from 0.01% to 2%, by weight of the composition. Mixtures of the compounds may also be used herein.

**[0077]** Incorporation of the amine reaction product in the laundry and cleaning compositions can conveniently be carried out, if necessary, by conventional incorporation means, such as by spray-on, encapsulation like starch encapsulation, e.g. as described in GB1464616, dry addition, or by encapsulation in cyclodextrin. Preferably, the amine reaction product is preformed before incorporation into the laundry and cleaning compositions. In other words, the perfume component and the amino functional polymer of the present invention are first reacted together to obtain the resulting amine reaction product as defined in the present invention and only once formed incorporated into the laundry and cleaning compositions. By being preformed before the incorporation in fully formulated composition, a better control of the compound being made is obtained. Hence, the interaction with perfume composition which may be present in fully formulated composition is avoided as well as side reaction that could occur. Further, by such means of incorporation, efficient control of the yield and purity of the compound is obtained.

**[0078]** Most preferably, when the laundry and cleaning composition comprises a perfume, the amine reaction product is incorporated in the composition separately from the perfume. By this means, the amine reaction product and its subsequent perfume release is more controlled.

**[0079]** Typically the laundry and cleaning composition comprises a deterative ingredient and further optional ingredients as described hereinafter as optional ingredients.

**Deterative ingredients**

**[0080]** Non-limiting examples of surfactants useful herein typically at levels from 1 % to 55%, by weight, include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C<sub>10</sub>-C<sub>20</sub> alkyl sulfates ("AS"), the C<sub>10</sub>-C<sub>18</sub> secondary (2,3) alkyl sulfates of the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub>(CHOSO<sub>3</sub><sup>-</sup> M<sup>+</sup>) CH<sub>3</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>y</sub>(CHOSO<sub>3</sub><sup>-</sup> M<sup>+</sup>) CH<sub>2</sub>CH<sub>3</sub> where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AES", especially x up to 7 EO ethoxy sulfates), C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C<sub>10</sub>-C<sub>18</sub> glycerol ethers, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, and C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, cationic surfactants and the like, can also be included in the overall compositions. The C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides can be used for low sudsing. C<sub>10</sub>-C<sub>20</sub> conventional soaps may also be used. If high sudsing is desired, the branched-chain C<sub>10</sub>-C<sub>16</sub> soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

**[0081]** Fully formulated laundry and cleaning compositions preferably contain, in addition to the hereinbefore described components, one or more of the following ingredients.

## **Builders**

**[0082]** Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

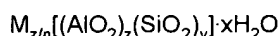
**[0083]** The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least 1% builder, preferably from 1% to 80%. Liquid formulations typically comprise from 5% to 50%, more typically 5% to 30%, by weight, of detergent builder. Granular formulations typically comprise from 1 % to 80%, more typically from 5% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

**[0084]** Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates, and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

**[0085]** Examples of silicate builders are the alkali metal silicates, particularly those having a SiO<sub>2</sub>:Na<sub>2</sub>O ratio in the range 1.0:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. 4,664,839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na<sub>2</sub>SiO<sub>5</sub> morphology form of layered silicate. It can be prepared by methods such as those described in DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi<sub>x</sub>O<sub>2x+1</sub>·yH<sub>2</sub>O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na<sub>2</sub>SiO<sub>5</sub> (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in DE 2,321,001.

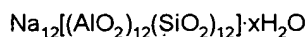
**[0086]** Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 0, and x is an integer from 0 to 264, and M is a Group IA or IIA element, e.g., Na, K, Mg, Ca with valence n.

**[0087]** Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange

material has the formula:



wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

[0088] Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

[0089] Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. 3,128,287, U.S. 3,635,830. See also "TMS/TDS" builders of U.S. 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

[0090] Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, pyromellitic, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

[0091] Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

[0092] Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263.

[0093] Other suitable polycarboxylates are disclosed in U.S. 4,144,226 and in U.S. 3,308,067. See also U.S. 3,723,322.

[0094] Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids such as oleic acid and/or its salts, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

[0095] In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

#### Bleaching Compounds - Bleaching Agents and Bleach Activators

[0096] The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from 1% to 30%, more typically from 5% to 20%, of the detergent composition, especially for fabric laundrying. If present, the amount of bleach activators will typically be from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

[0097] The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents like hypochlorite bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein. When hypochlorite is used, a highly preferred hypochlorite bleaching component is an alkali metal hypochlorite. Although alkali metal hypochlorites are preferred, other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite.

[0098] Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S. 740,446, EP 0,133,354, and U.S. 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. 4,634,551.

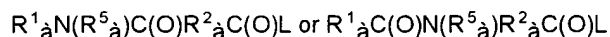
**[0099]** Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

**[0100]** A preferred percarbonate bleach comprises dry particles having an average particle size in the range from 500 micrometers to 1,000 micrometers, not more than 10% by weight of said particles being smaller than 200 micrometers and not more than 10% by weight of said particles being larger than 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

**[0101]** Mixtures of bleaching agents can also be used.

**[0102]** Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. 4,915,854, and U.S. 4,412,934. The nonanoyloxybenzene sulfonate (NOBS), 3,5,5-tri-methyl hexanoyl oxybenzene sulfonate (ISONOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

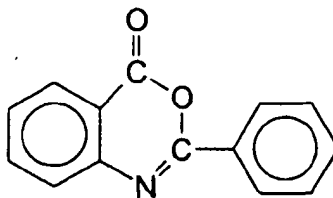
Highly preferred amido-derived bleach activators are those of the formulae:



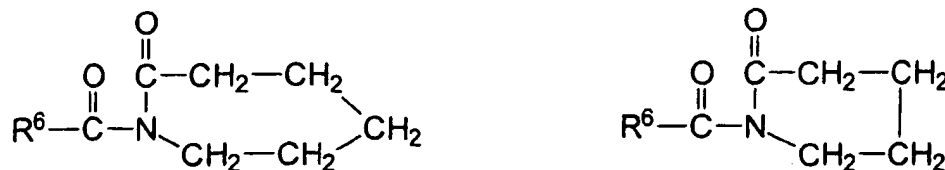
wherein  $R^1_{\text{a}}$  is an alkyl group containing from 6 to 12 carbon atoms,  $R^2_{\text{a}}$  is an alkylene containing from 1 to 6 carbon atoms,  $R^5_{\text{a}}$  is H or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

**[0103]** Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

**[0104]** Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723. A highly preferred activator of the benzoxazin-type is:



**[0105]** Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein R<sup>6</sup><sub>a</sub> is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

**[0106]** Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. 4,033,718. If used, detergent compositions will typically contain from 0.025% to 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

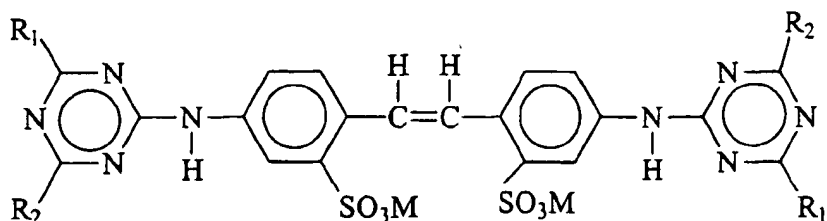
**[0107]** If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well-known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5, 246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP 549,271A1, 549,272A1, 544,440A2, and 544,

490A1; Preferred examples of these catalysts include  $\text{Mn}^{\text{IV}}_{\text{a}_2}(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_{\text{a}_2}(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_{\text{a}_4}(\text{u-O})_6(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_4(\text{ClO}_4)_4$ ,  $\text{Mn}^{\text{III}}_{\text{a}}\text{Mn}^{\text{IV}}_{\text{a}_4}(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$ ,  $\text{Mn}^{\text{IV}}_{\text{a}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_3(\text{OCH}_3)_3(\text{PF}_6)_3$ , and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following US Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

**[0108]** As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from 0.1 ppm to 700 ppm, more preferably from 1 ppm to 500 ppm, of the catalyst species in the laundry liquor.

#### Brighteners

**[0109]** The compositions herein can also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.001% to 1 % by weight of such optical brighteners. The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein  $R_1$  is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl;  $R_2$  is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula,  $R_1$  is anilino,  $R_2$  is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX® by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the rinse added compositions herein.

When in the above formula,  $R_1$  is anilino,  $R_2$  is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX® by Ciba-Geigy Corporation.

When in the above formula,  $R_1$  is anilino,  $R_2$  is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX® by Ciba Geigy Corporation.

#### Soil Release Agent

**[0110]** In the present invention, an optional soil release agent can be added. Typical levels of incorporation in the composition are from 0% to 10%, preferably from 0.2% to 5%, of a soil release agent. Preferably, such a soil release agent is a polymer.

**[0111]** Soil Release agents are desirably used in fabric softening compositions of the instant invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

**[0112]** If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

**[0113]** The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, *et al.*, issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel *et al.*, issued November 6; U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado *et al.*, issued October 31, 1989; U.S. 4,956,447, Gosselink *et al.*, issued September 11, 1990; U.S. 5,415,



807 Gosselink *et al.*, issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, *et al.*

[0114] Further suitable soil release agents are described in U.S. 4,201,824, Violland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681, Ruppert *et al.*; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

[0115] Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

#### Scum Dispersant

[0116] In the present invention, the premix can be combined with an optional scum dispersant, other than the soil release agent, and heated to a temperature at or above the melting point(s) of the components.

The preferred scum dispersants herein are formed by highly ethoxylating hydrophobic materials. The hydrophobic material can be a fatty alcohol, fatty acid, fatty amine, fatty acid amide, amine oxide, quaternary ammonium compound, or the hydrophobic moieties used to form soil release polymers. The preferred scum dispersants are highly ethoxylated, e.g., more than 17, preferably more than 25, more preferably more than 40, moles of ethylene oxide per molecule on the average, with the polyethylene oxide portion being from 76% to 97%, preferably from 81% to 94%, of the total molecular weight. The level of scum dispersant is sufficient to keep the scum at an acceptable, preferably unnoticeable to the consumer, level under the conditions of use, but not enough to adversely affect softening. For some purposes it is desirable that the scum is nonexistent. Depending on the amount of anionic or nonionic detergent, etc., used in the wash cycle of a typical laundering process, the efficiency of the rinsing steps prior to the introduction of the compositions herein, and the water hardness, the amount of anionic or nonionic detergent surfactant and detergency builder (especially phosphates and zeolites) entrapped in the fabric (laundry) will vary. Normally, the minimum amount of scum dispersant should be used to avoid adversely affecting softening properties. Typically scum dispersion requires at least 2%, preferably at least 4% (at least 6% and preferably at least 10% for maximum scum avoidance) based upon the level of softener active. However, at levels of 10% (relative to the softener material) or more, one risks loss of softening efficacy of the product especially when the fabrics contain high proportions of nonionic surfactant which has been absorbed during the washing operation.

Preferred scum dispersants are: Brij 700®; Varonic U-250®; Genapol T-500®, Genapol T-800®, Plurafac A-79®, and Neodol 25-50®.

#### Bactericides

[0117] Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon 1 to 1,000 ppm by weight of the agent.

#### Perfume

[0118] The present invention can contain any detergent compatible perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpeneol; 3,7-dimethyl-cis-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecanyl propionate; tricyclodecanyl acetate; anisaldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methylether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbonyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecandioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododecatien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane;

benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolate; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; olibanum resinoid; labdanum; vetiver; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl methylphenylcarbinyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentyl-cyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionones; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution. Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

#### Chelating Agents

**[0119]** The compositions and processes herein can optionally employ one or more copper and/or nickel chelating agents ("chelators"). Such water-soluble chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. The whiteness and/or brightness of fabrics are substantially improved or restored by such chelating agents and the stability of the materials in the compositions are improved. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

**[0120]** Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

**[0121]** Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

**[0122]** Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzene such as 1,2-dihydroxy-3,5-disulfobenzene.

**[0123]** A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

**[0124]** The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

**[0125]** Preferred chelating agents include DETMP, DETPA, NTA, EDDS and mixtures thereof.

**[0126]** If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the fabric care compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

#### Crystal growth inhibitor component

**[0127]** The compositions of the present invention can further contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the compositions.

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[0128] By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

[0129] The organo diphosphonic acid is preferably a C<sub>1</sub>-C<sub>4</sub> diphosphonic acid, more preferably a C<sub>2</sub> diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

[0130] Still useful herein as crystal growth inhibitor are the organic monophosphonic acid  
Organo monophosphonic acid or one of its salts or complexes is also suitable for use herein as a CGI.

[0131] By organo monophosphonic acid it is meant herein an organo monophosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrants.

[0132] The organo monophosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

[0133] A preferred organo monophosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer under the tradename of Bayhibit.

### Enzyme

[0134] The compositions and processes herein can optionally employ one or more enzymes such as lipases, proteases, cellulase, amylases and peroxidases. A preferred enzyme for use herein is a cellulase enzyme. Indeed, this type of enzyme will further provide a color care benefit to the treated fabric. Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. Other suitable cellulases are also disclosed in WO 91/17243 to Novo, WO 96/34092, WO 96/34945 and EP-A-0,739,982. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. In the particular cases where activity of the enzyme preparation can be defined otherwise such as with cellulases, corresponding activity units are preferred (e.g. CEVU or cellulase Equivalent Viscosity Units). For instance, the compositions of the present invention can contain cellulase enzymes at a level equivalent to an activity from 0.5 to 1000 CEVU/gram of composition. Cellulase enzyme preparations used for the purpose of formulating the compositions of this invention typically have an activity comprised between 1,000 and 10,000 CEVU/gram in liquid form, around 1,000 CEVU/gram in solid form.

[0135] Other preferred optional ingredients include enzyme stabilisers, polymeric soil release agents, materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process (i.e., dye transfer inhibiting agents), polymeric dispersing agents, suds suppressors, optical brighteners or other brightening or whitening agents, chelating agents, fabric softening clay, anti-static agents, other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations and solid fillers for bar compositions.

[0136] Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

[0137] Granular detergents can be prepared, for example, by spray-drying (final product density 520 g/l) or agglomerating (final product density above 600 g/l) the Base Granule. The remaining dry ingredients can then be admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.

[0138] The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well-known to those skilled in the art.

### Method of use

[0139] Also provided herein is a method for providing a delayed release of an active ketone or aldehyde which comprises the step of contacting the surface to be treated with a compound or composition of the invention, and thereafter contacting the treated surface with a material, preferably an aqueous medium like moisture or any other means susceptible of releasing the perfume from the amine reaction product.

[0140] By "surface", it is meant any surface onto which the compound can deposit. Typical examples of such material are fabrics, hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of a perfume ketone and/or aldehyde such as that with litter like animal litter. Preferably, the surface is selected from a fabric, a tile, a ceramic; more preferably is a fabric.

**[0141]** By "delayed release" is meant release of the active component (e.g perfume) over a longer period of time than by the use of the active (e.g., perfume) itself.

Abbreviations used in the following laundry and cleaning composition Examples

**[0142]** In the laundry and cleaning compositions, the abbreviated component identifications have the following meanings:

**[0143]** In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	Sodium linear C <sub>11-13</sub> alkyl benzene sulfonate
TAS	Sodium tallow alkyl sulfate
CxyAS	Sodium C <sub>1x</sub> -C <sub>1y</sub> alkyl sulfate
C46SAS	Sodium C <sub>14</sub> -C <sub>16</sub> secondary (2,3) alkyl sulfate
CxyEzS	Sodium C <sub>1x</sub> -C <sub>1y</sub> alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	C <sub>1x</sub> -C <sub>1y</sub> predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	R <sub>2</sub> .N <sup>+</sup> <sub>a</sub> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> - C <sub>14</sub>
QAS 1	R <sub>2</sub> .N <sup>+</sup> <sub>a</sub> (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>8</sub> - C <sub>11</sub>
APA	C <sub>8</sub> - C <sub>10</sub> amido propyl dimethyl amine
Soap	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	Sodium toluene sulphonate
CFAA	C <sub>12</sub> -C <sub>14</sub> (coco) alkyl N-methyl glucamide
TFAA	C <sub>16</sub> -C <sub>18</sub> alkyl N-methyl glucamide
TPKFA	C <sub>12</sub> -C <sub>14</sub> topped whole cut fatty acids
STPP	Anhydrous sodium tripolyphosphate
TSPP	Tetrasodium pyrophosphate
Zeolite A	Hydrated sodium aluminosilicate of formula Na <sub>12</sub> (AlO <sub>2</sub> SiO <sub>2</sub> ) <sub>12</sub> .27H <sub>2</sub> O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
NaSKS-6	Crystalline layered silicate of formula δ-Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>
Citric acid	Anhydrous citric acid
Borate	Sodium borate
Carbonate	Anhydrous sodium carbonate with a particle size between 200µm and 900µm
Bicarbonate	Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm
Silicate	Amorphous sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 2.0:1)
Sulfate	Anhydrous sodium sulfate
Mg sulfate	Anhydrous magnesium sulfate
Citrate	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
MA/AA	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA(1)	Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
AA	Sodium polyacrylate polymer of average molecular weight 4,500
CMC	Sodium carboxymethyl cellulose
Cellulose ether	Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
Protease	Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
Protease I	Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
Alcalase	Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
Cellulase	Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme

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	Amylase	Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Termamyl 120T
	Lipase	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
5	Lipase (1)	Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
	Endolase	Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
	PB4	Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
10	PB1	Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
	Percarbonate	Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
	NOBS	Nonanoyloxybenzene sulfonate in the form of the sodium salt
	NAC-OBS	(6-nonamidocaproyl) oxybenzene sulfonate
	TAED	Tetraacetythylenediamine
15	DTPA	Diethylene triamine pentaacetic acid
	DTPMP	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
	EDDS	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
20	Photoactivated bleach (1)	Sulfonated zinc phthlocyanine encapsulated in dextrin soluble polymer
	Photoactivated bleach (2)	Sulfonated alumino phthlocyanine encapsulated in dextrin soluble polymer
	Brightener 1	Disodium 4,4'-bis(2-sulphostyryl) biphenyl
25	Brightener 2	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino stilbene-2:2'-disulfonate
	HEDP	1,1-hydroxyethane diphosphonic acid
	PEGx	Polyethylene glycol, with a molecular weight of x (typically 4,000)
	PEO	Polyethylene oxide, with an average molecular weight of 50,000
	TEPAE	Tetraethylenepentaamine ethoxylate
30	PVI	Polyvinyl imidosole, with an average molecular weight of 20,000
	PVP	Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
	PVNO	Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
	PVPVI	Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
35	QEA	$\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) \cdot \text{N}^+ \text{--} \text{C}_6\text{H}_{12} \text{--} \text{N}^+ \text{--} (\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O}))_n$ , wherein n = from 20 to 30
	SRP 1	Anionically end capped poly esters
	SRP 2	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
40	PEI	Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
	Silicone antifoam	Polydimethylsiloxane foam controller with siloxaneoxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
45	Opacifier	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
	Wax	Paraffin wax
	PA30	Polyacrylic acid of average molecular weight of between about 4,500 - 8,000.
	480N	Random copolymer of 7:3 acrylate/methacrylate, average molecular weight about 3,500.
	Polygel/carbopol	High molecular weight crosslinked polyacrylates.
50	Metasilicate	Sodium metasilicate ( $\text{SiO}_2 \cdot \text{Na}_2\text{O}$ ratio = 1.0).
	Nonionic	$\text{C}_{13}\text{--}\text{C}_{15}$ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
	Neodol 45-13	$\text{C}_{14}\text{--}\text{C}_{15}$ linear primary alcohol ethoxylate, sold by Shell Chemical CO.
55	MnTACN	Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.
	PAAC	Pentaamine acetate cobalt(III) salt.
	Paraffin	Paraffin oil sold under the tradename Winog 70 by Wintershall.

NaBz	Sodium benzoate.
BzP	Benzoyl Peroxide.
SCS	Sodium cumene sulphonate.
BTB	Benzotriazole.
pH	Measured as a 1% solution in distilled water at 20°C.
ARP1	Amine reaction product of 1,4-bis-(3-aminopropyl)-piperazine with $\alpha$ -Damascone as made from Synthesis example I
ARP2	Amine reaction product of N,N'-bis(aminopropyl)-1,3-propanediamine with $\delta$ -Damascone as made from Synthesis example II
ARP3	Amine reaction product of polyvinylamine MW1200 with $\alpha$ -Damascone as made from Synthesis example III

[0144] The following are synthesis examples of compounds as defined in the present invention:

I-Synthesis of 1,4-bis-(3-aminopropyl)-piperazine with  $\alpha$ -Damascone

[0145] In order to substitute both primary amine groups with a perfume, 2eq of perfume were used for 1eq of amino functional polymer. To an ice cooled stirred solution of 1mmol of  $\alpha$ -Damascone in 6 mL EtOH and molecular sieves (4A, 20 g), 0.5eq of 1,4-bis-(3-aminopropyl)-piperazine was added via an addition funnel. The reaction mixture was stirred under nitrogen atmosphere and protected from light. After the disappearance of the absorption peak from the NMR spectrum of the free perfume raw material (from 3 to 16 hours), the mixture was filtrated and the solvent was removed by vacuum distillation. The yield of  $\beta$ -aminoketone formation is about 90%.

[0146] Similar results were obtained where the  $\alpha$ -Damascone was replaced by Tripal, vertocitral, bourgeonal, or citronellal. In these instances, Schiff-bases are formed.

II-Synthesis of N,N'-bis(3-aminopropyl)-1,3-propanediamine with  $\delta$ -Damascone

[0147] To an ice cooled solution of 1 mmol of  $\delta$ -Damascone in 30 mL EtOH and molecular sieves (4Å, 5 g), 0.5eq of the N,N'-bis(3-aminopropyl)-1,3-propanediamine was added. The reaction was stirred under nitrogen atmosphere and protected from light. After 1 day, the molecular sieves and the solvent were removed by filtration and vacuum distillation respectively.  $\beta$ -Aminoketone were obtained in a 85 to 90% yield.

[0148] Similar results were obtained where the  $\delta$ -Damascone was replaced by Tripal, vertocitral, bourgeonal, or citronellal. In these instances, Schiff-bases are formed.

III-Synthesis of Polyvinylamine of MW1200 with  $\alpha$ -Damascone

[0149] The following ingredients were mixed together : 0.6g of Sodium sulfate with 0.3g of polyvinylamine MW 1200 in a 10% aqueous solution and 0.3g  $\alpha$ -Damascone. The reaction was completed after 18 days at room temperature in the dark.

[0150] Similar results were obtained where the  $\alpha$ -Damascone was replaced by Tripal, or citral. In these instances, Schiff-bases are formed.

[0151] In the following formulation examples all levels are quoted as % by weight of the composition unless otherwise stated, and incorporation of the amine reaction product so called herein after "ARP" in the fully formulated composition is carried out by dry addition (d), spray on (s), encapsulation in starch (es) as described in GB-1,464,616 or cyclodextrin (ec) or as is in the composition as defined herein before. The term in bracket for the ARP in the formulation examples refers to the means of incorporation. When none is provided, the incorporation is made as it is.

Example 1

[0152] The following high density granular laundry detergent compositions A to F were prepared in accord with the invention:

	A	B	C	D	E	F
LAS	8.0	8.0	8.0	2.0	6.0	6.0
TAS	-	0.5	-	0.5	1.0	0.1
C46(S)AS	2.0	2.5	-	-	-	-
C25AS	-	-	-	7.0	4.5	5.5
C68AS	2.0	5.0	7.0	-	-	-

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	A	B	C	D	E	F
C25E5	-	-	3.4	10.0	4.6	4.6
C25E7	3.4	3.4	1.0	-	-	-
C25E3S	-	-	-	2.0	5.0	4.5
QAS	-	0.8	-	-	-	-
QAS (I)	-	-	-	0.8	0.5	1.0
Zeolite A	18.1	18.0	14.1	18.1	20.0	18.1
Citric acid	-	-	-	2.5	-	2.5
Carbonate	13.0	13.0	27.0	10.0	10.0	13.0
SKS-6	-	-	-	10.0	-	10.0
Silicate	1.4	1.4	3.0	0.3	0.5	0.3
Citrate	-	1.0	-	3.0	-	-
Sulfate	26.1	26.1	26.1	6.0	-	-
Mg sulfate	0.3	-	-	0.2	-	0.2
MA/AA	0.3	0.3	0.3	4.0	1.0	1.0
CMC	0.2	0.2	0.2	0.2	0.4	0.4
PB4	9.0	9.0	5.0	-	-	-
Percarbonate	-	-	-	-	18.0	18.0
TAED	1.5	0.4	1.5	-	3.9	4.2
NAC-OBS	-	2.0	1.0	-	-	-
DTPMP	0.25	0.25	0.25	0.25	-	-
SRP 2	-	-	-	0.2	-	0.2
EDDS	-	0.25	0.4	-	0.5	0.5
CFAA	-	1.0	-	2.0	-	-
HEDP	0.3	0.3	0.3	0.3	0.4	0.4
QEA	-	-	-	0.2	-	0.5
Protease I	-	-	0.26	1.0	-	-
Protease	0.26	0.26	-	-	1.5	1.0
Cellulase	0.3	-	-	0.3	0.3	0.3
Amylase	0.1	0.1	0.1	0.4	0.5	0.5
Lipase (1)	0.3	-	-	0.5	0.5	0.5
Photoactivated bleach (ppm)	15 ppm	15 ppm	15ppm	-	20 ppm	20 ppm
PVNO/PVPVI	-	-	-	0.1	-	-
Brightener 1	0.09	0.09	0.09	-	0.09	0.09
Perfume spray on	0.3	0.3	0.3	0.4	0.4	0.4
ARP 1	0.03(d)	0.1(es)	-	-	0.1(d)	0.05(ec)
ARP 2	-	-	0.04(s)	0.04(ec)	0.02(s)	-
Silicone antifoam	0.5	0.5	0.5	-	0.3	0.3
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

[0153] The following granular laundry detergent compositions G to L of particular utility under European machine wash conditions were prepared in accord with the invention:

	G	H	I	J	K	L
LAS	5.5	7.5	5.0	5.0	6.0	7.0
TAS	1.25	1.86	-	0.8	0.4	0.3
C24AS/C25AS	-	2.24	5.0	5.0	5.0	2.2

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	<b>G</b>	<b>H</b>	<b>I</b>	<b>J</b>	<b>K</b>	<b>L</b>
C25E3S	-	0.76	1.0	1.5	3.0	1.0
C45E7	3.25	-	-	-	-	3.0
TFAA	-	-	2.0	-	-	-
C25E5	-	5.5	-	-	-	-
QAS	0.8	-	-	-	-	-
QAS II	-	0.7	1.0	0.5	1.0	0.7
STPP	19.7	-	-	-	-	-
Zeolite A	-	19.5	25.0	19.5	20.0	17.0
NaSKS-6/citric acid (79:21)	-	10.6	-	10.6	-	-
NaSKS-6	-	-	9.0	-	10.0	10.0
Carbonate	6.1	21.4	9.0	10.0	10.0	18.0
Bicarbonate	-	2.0	7.0	5.0	-	2.0
Silicate	6.8	-	-	0.3	0.5	-
Citrate	-	-	4.0	4.0	-	-
Sulfate	39.8	-	-	5.0	-	12.0
Mg sulfate	-	-	0.1	0.2	0.2	-
MA/AA	0.5	1.6	3.0	4.0	1.0	1.0
CMC	0.2	0.4	1.0	1.0	0.4	0.4
PB4	5.0	12.7	-	-	-	-
Percarbonate	-	-	-	-	18.0	15.0
TAED	0.5	3.1	-	-	5.0	-
NAC-OBS	1.0	3.5	-	-	-	2.5
DTPMP	0.25	0.2	0.3	0.4	-	0.2
HEDP	-	0.3	-	0.3	0.3	0.3
QEA	-	-	1.0	1.0	1.0	-
Protease I	-	-	-	0.5	1.2	-
Protease	0.26	0.85	0.9	1.0	-	0.7
Lipase (1)	0.15	0.15	0.3	0.3	0.3	0.2
Cellulase	0.28	0.28	0.2	0.2	0.3	0.3
Amylase	0.1	0.1	0.4	0.4	0.6	0.2
PVNO/PVPVl	-	-	0.2	0.2	-	-
PVP	0.9	1.3	-	-	-	0.9
SRP 1	-	-	0.2	0.2	0.2	-
Photoactivated bleach (1) in ppm	15	27	-	-	20	20
Photoactivated bleach (2) in ppm	15	-	-	-	-	-
Brightener 1	0.08	0.19	-	-	0.09	0.15
Brightener 2	-	0.04	-	-	-	-
Perfume	0.3	0.3	0.4	0.3	0.4	0.3
ARP1	0.1(d) 0.1(es)	1.0(d)	-	-	-	0.1(es)
ARP2	-	-	0.04(s)	0.02(ec)	0.04(d)	0.02(es)
Silicone antifoam	0.5	2.4	0.3	0.5	0.3	2.0
Minors/misc to 100%						
Density in g/litre	750	750	750	750	750	750

Example 3

**[0154]** The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.



**EP 0 971 026 A1**

	M	N	O	P
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-
MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
EDDS	0.3	-	-	-
Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
Citric acid	2.5	-	-	2.0
QAS II	0.5	-	-	0.5
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NAC-OBS	3.0	2.0	4.0	-
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
ARP3	0.03	0.1(es)	1.0	0.1 0.05(ec)
Misc/minor to 100%				

**Example 4**

**[0155]** The following granular detergent formulations were prepared in accord with the invention.

	Q	R	S	T	U	V
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-

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	Q	R	S	T	U	V
Blown powder						
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA(1)	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
ARP5	0.1(s)	0.05(s)	-	-	-	-
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
ARP2	0.1	0.2	0.04(d)	0.02	0.01(es)	0.02(es)
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Misc/minors to 100%						

Example 5

[0156] The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
ARP2	0.04(s)	-	-
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0 m	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
ARP1	0.05	0.08	0.1(es)
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

Example 6

[0157] The following granular detergent formulations were prepared in accord with the invention.

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	Z	AA	BB	CC
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA(1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
ARP2	0.04(s)	-	-	-
Dry additives				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	1.0	1.0	1.0	0.5
Lipase	0.4	-	-	0.4
Amylase	0.1	-	-	0.1
Cellulase	0.1	0.2	0.2	0.1
NOBS	-	4.0	-	4.5
PB1	1.0	5.0	1.5	6.0
Sulfate	4.0	5.0	-	5.0
SRPI	-	0.4	-	-
ARP1	0.05	0.08	0.1(es)	-
ARP2	0.05	-	-	0.02(es)
Sud supressor	-	0.5	0.5	-
Misc/minor to 100%				

Example 7

**[0158]** The following granular detergent compositions were prepared in accord with the invention.

	DD	EE	FF
Blown powder			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sulphate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0

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	DD	EE	FF
Blown powder			
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DTPMP	0.4	0.4	0.1
STS	-	-	1.0
Spray on			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
ARP1	0.1(s)	0.05(s)	0.08(s)
Dry additives			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-
PB4	18.5	13.0	13.0
TAED	2.0	2.0	2.0
QAS (I)	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15ppm
SKS-6	-	-	3.0
Protease	1.0	1.0	0.2
Lipase	0.2	0.2	0.2
Amylase	0.4	0.4	0.2
Cellulase	0.1	0.1	0.2
Sulfate	10.0	20.0	5.0
Misc/minors to 100%			
Density (g/litre)	700	700	700

**Example 8**

**[0159]** The following detergent compositions, according to the present invention were prepared:

	GG	HH	II
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0

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	GG	HH	II
Agglomerates			
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
ARP2	0.02(s)	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
PEO	-	-	0.2
ARP1	0.1	0.2	0.08(ec)
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 9

**[0160]** The following detergent formulations, according to the present invention were prepared:

	JJ	KK	LL	MM
LAS	18.0	14.0	24.0	20.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C23E56.5	-	-	1.0	-
C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	32.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	11.0	7.5	10.0	5.0
Bicarbonate	-	7.5	-	-
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
NOBS	2.0	1.0	-	-
DTPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2

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	JJ	KK	LL	MM
PEI	-	-	0.4	-
Sodium sulfate	20.0	10.0	20.0	30.0
Mg sulfate	0.2	-	0.4	0.9
Protease	0.8	1.0	0.5	0.5
Amylase	0.5	0.4	-	0.25
Lipase	0.2	-	0.1	-
Cellulase	0.15	-	-	0.05
Photoactivated bleach (ppm)	30ppm	20ppm	-	10ppm
ARP3	0.04(s)	0.02(ec)	0.1(s)	0.01(es)
Perfume spray on	0.3	0.3	0.1	0.2
Brightener 1/2	0.05	0.2	0.08	0.1
Misc/minors to 100%				

Example 10

**[0161]** The following liquid detergent formulations were prepared in accord with the invention (levels are given as parts per weight).

	NN	OO	PP	QQ	RR
LAS	11.5	8.8	-	3.9	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric acid (50%)	6.5	1.2	2.5	4.4	2.5
Calcium formate	0.1	0.06	0.1	-	-
Sodium formate	0.5	0.06	0.1	0.05	0.05
Sodium cumene sulfonate	4.0	1.0	3.0	1.18	-
Borate	0.6	-	3.0	2.0	2.9
Sodium hydroxide	5.8	2.0	3.5	3.7	2.7
Ethanol	1.75	1.0	3.6	4.2	2.9
1, 2 propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Protease	1.0	0.3	1.0	0.5	0.7
Lipase	-	-	0.1	-	-
Cellulase	-	-	0.1	0.2	0.05
Amylase	-	-	-	0.1	-
SRP1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
ARP1	0.3	-	-	0.1	-
ARP2	-	0.04	-	-	0.1
ARP3	-	-	0.3	-	-
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Water/minors					

## Example 11

[0162] The following liquid detergent formulations were prepared in accord with the invention (levels are given in parts per weight):

	SS	TT	UU	VV	WW	XX	YY	ZZ
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodeceny/tetradeceny succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rape seed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	-	-
TEPAE	0.5	-	0.5	0.2	-	-	0.4	0.3
DTPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-
Lipase	-	0.10	-	0.01	-	-	0.15	0.15
Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15
Endolase	-	-	-	0.10	-	-	0.07	-
SRP2	0.3	-	0.3	0.1	-	-	0.2	0.1
Boric acid	0.1	0.2	1.0	2.0	1.0	1.5	2.5	2.5
Calcium chloride	-	0.02	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Brightener 1	-	0.4	-	-	0.1	0.2	0.3	-
Sud supressor	0.1	0.3	-	0.1	0.4	-	-	-
Opacifier	0.5	0.4	-	0.3	0.8	0.7	-	-
ARP1	0.3	-	0.1	-	0.05	-	0.1	0.08
ARP2	-	0.04	-	0.02	-	0.1	0.02	0.1
Water/minors								
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2

## Example 12

[0163] The following liquid detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	AB	AC
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
Oleic acid	3.4	2.5



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	AB	AC
Citric acid	5.4	5.4
Sodium hydroxide	0.4	3.6
Calcium formate	0.2	0.1
Sodium formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	1.5	0.6
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume spray on	0.5	0.3
ARP1	0.3	-
ARP3	-	0.04
Water/minors		

Example 13

**[0164]** The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	AD	AE	AF	AG	AH	AI	AJ	AK
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Sodium laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Calcium carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DTPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	-	-	0.1
Lipase	-	0.1	-	0.1	-	-	-	-
Amylase	-	-	0.8	-	-	-	0.1	-
Cellulase	-	0.15	-	-	0.15	0.1	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
ARP1	0.3	-	-	0.04	-	0.5	-	-
ARP2	-	0.04	-	-	0.1	-	0.08	-

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	AD	AE	AF	AG	AH	AI	AJ	AK
ARP3	-	-	0.3	-	-	-	-	0.3
Brightener	0.15	0.10	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

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Example 14

10 **[0165]** The following detergent additive compositions were prepared according to the present invention :

	AL	AM	AN
LAS	-	5.0	5.0
STPP	30.0	-	20.0
Zeolite A	-	35.0	20.0
PB1	20.0	15.0	-
TAED	10.0	8.0	-
ARP1	0.3	-	0.1
ARP2	-	0.04	0.02
Protease	-	0.3	0.3
Amylase	-	0.06	0.06
Minors, water and miscellaneous		Up to 100%	

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Example 15

30 **[0166]** The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	AO	AP	AQ	AR	AS	AT	AU	AV
STPP	-	-	54.3	51.4	51.4	-	-	50.9
Citrate	35.0	17.0	-	-	-	46.1	40.2	-
Carbonate	-	17.5	14.0	14.0	14.0	-	8.0	32.1
Bicarbonate	-	-	-	-	-	25.4	-	-
Silicate	32.0	14.8	14.8	10.0	10.0	1.0	25.0	3.1
Metasilicate	-	2.5	-	9.0	9.0	-	-	-
PB1	1.9	9.7	7.8	7.8	7.8	-	-	-
PB4	8.6	-	-	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7	11.8	4.8
Nonionic	1.5	2.0	1.5	1.7	1.5	2.6	1.9	5.3
TAED	5.2	2.4	-	-	-	2.2	-	1.4
HEDP	-	1.0	-	-	-	-	-	-
DTPMP	-	0.6	-	-	-	-	-	-
MnTACN	-	-	-	-	-	-	0.008	-
PAAC	-	-	0.008	0.01	0.007	-	-	-
BzP	-	-	-	-	1.4	-	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.6	-	-
ARP3	0.1	0.3	0.2	0.05	-	-	-	0.8
ARP1	-	-	-	-	0.3	0.03	0.5	-
Protease	0.072	0.072	0.029	0.053	0.046	0.026	0.059	0.06
Amylase	0.012	0.012	0.006	0.012	0.013	0.009	0.017	0.03
Lipase	-	0.001	-	0.005	-	-	-	-

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	AO	AP	AQ	AR	AS	AT	AU	AV
BTA	0.3	0.3	0.3	0.3	0.3	-	0.3	0.3
MA/AA	-	-	-	-	-	-	4.2	-
480N	3.3	6.0	-	-	-	-	-	0.9
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1
Sulphate	7.0	20.0	5.0	2.2	0.8	12.0	4.6	-
pH	10.8	11.0	10.8	11.3	11.3	9.6	10.8	10.9
Miscellaneous and water	Up to 100%							

**Example 16**

**[0167]** The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

	AW	AX	AY	AZ	BA	BC	BD	BE
STPP	30.0	30.0	33.0	34.2	29.6	31.1	26.6	17.6
Carbonate	30.5	30.5	31.0	30.0	23.0	39.4	4.2	45.0
Silicate	7.4	7.4	7.5	7.2	13.3	3.4	43.7	12.4
Metasilicate	-	-	4.5	5.1	-	-	-	-
Percarbonate	-	-	-	-	-	4.0	-	-
PB1	4.4	4.2	4.5	4.5	-	-	-	-
NADCC	-	-	-	-	2.0	-	1.6	1.0
Nonionic	1.2	1.0	0.7	0.8	1.9	0.7	0.6	0.3
TAED	1.0	-	-	-	-	0.8	-	-
PAAC	-	0.004	0.004	0.004	-	-	-	-
BzP	-	-	-	1.4	-	-	-	-
Paraffin	0.25	0.25	0.25	0.25	-	-	-	-
ARP3	0.3	0.1(ec)	0.8	0.2(es)	-	-	0.1(ec)	0.2
ARP1	-	-	-	-	0.3	0.1(ec)	0.1(ec)	0.2
Protease	0.036	0.015	0.03	0.028	-	0.03	-	-
Amylase	0.003	0.003	0.01	0.006	-	0.01	-	-
Lipase	0.005	-	0.001	-	-	-	-	-
BTA	0.15	0.15	0.15	0.15	-	-	-	-
Perfume	0.2	0.2	0.2	0.2	0.1	0.2	0.2	-
Sulphate	23.4	25.0	22.0	18.5	30.1	19.3	23.1	23.6
pH	10.8	10.8	11.3	11.3	10.7	11.5	12.7	10.9
Miscellaneous and water	Up to 100%							

**Example 17**

**[0168]** The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm<sup>2</sup> using a standard 12 head rotary press:

	BF	BJ	BK	BL	BM	BN
STPP	-	48.8	49.2	38.0	-	46.8
Citrate	26.4	-	-	-	31.1	-
Carbonate	-	5.0	14.0	15.4	14.4	23.0
Silicate	26.4	14.8	15.0	12.6	17.7	2.4

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	BF	BJ	BK	BL	BM	BN
ARP1	0.3	-	-	-	0.06	-
ARP2	-	0.04	-	-	-	0.08
ARP3	-	-	0.3	0.1(ec)	-	-
Protease	0.058	0.072	0.041	0.033	0.052	0.013
Amylase	0.01	0.03	0.012	0.007	0.016	0.002
Lipase	0.005	-	-	-	-	-
PB1	1.6	7.7	12.2	10.6	15.7	-
PB4	6.9	-	-	-	-	14.4
Nonionic	1.5	2.0	1.5	1.65	0.8	6.3
PAAC	-	-	0.02	0.009	-	-
MnTACN	-	-	-	-	0.007	-
TAED	4.3	2.5	-	-	1.3	1.8
HEDP	0.7	-	-	0.7	-	0.4
DTPMP	0.65	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.55	-	-
BTA	0.2	0.3	0.3	0.3	-	-
PA30	3.2	-	-	-	-	-
MA/AA	-	-	-	-	4.5	0.55
Perfume	-	-	0.05	0.05	0.2	0.2
Sulphate	24.0	13.0	2.3	-	10.7	3.4
Weight of tablet	25g	25g	20g	30g	18g	20g
pH	10.6	10.6	10.7	10.7	10.9	11.2
Miscellaneous and water	Up to 100%					

**Example 18**

**[0169]** The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

	BO	BP	BQ	BR
STPP	17.5	17.5	17.2	16.0
Carbonate	2.0	-	2.4	-
Silicate	5.3	6.1	14.6	15.7
NaOCl	1.15	1.15	1.15	1.25
Polygen/carbopol	1.1	1.0	1.1	1.25
Nonionic	-	-	0.1	-
NaBz	0.75	0.75	-	-
ARP3	0.3	0.5	0.05	0.1
NaOH	-	1.9	-	3.5
KOH	2.8	3.5	3.0	-
pH	11.0	11.7	10.9	11.0
Sulphate, miscellaneous and water	up to 100%			

**Example 19**

**[0170]** The following liquid rinse aid compositions were prepared according to the present invention :

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	BS	BT	BU
Nonionic	12.0	-	14.5
Nonionic blend	-	64.0	-
Citric	3.2	-	6.5
HEDP	0.5	-	-
PEG	-	5.0	-
SCS	4.8	-	7.0
Ethanol	6.0	8.0	-
ARP1	0.3	-	0.1
ARP2	-	0.04	0.01
pH of the liquid	2.0	7.5	/
Miscellaneous and water	Up to 100%		

**Example 20**

**[0171]** The following liquid dishwashing compositions were prepared according to the present invention :

	BV	BW	BX	BY	BZ
C17ES	28.5	27.4	19.2	34.1	34.1
Amine oxide	2.6	5.0	2.0	3.0	3.0
C12 glucose amide	-	-	6.0	-	-
Betaine	0.9	-	-	2.0	2.0
Xylene sulfonate	2.0	4.0	-	2.0	-
Neodol C11E9	-	-	5.0	-	-
Polyhydroxy fatty acid amide	-	-	-	6.5	6.5
Sodium diethylene penta acetate (40%)	-	-	0.03	-	-
TAED	-	-	-	0.06	0.06
Sucrose	-	-	-	1.5	1.5
Ethanol	4.0	5.5	5.5	9.1	9.1
Alkyl diphenyl oxide disulfonate	-	-	-	-	2.3
Ca formate	-	-	-	0.5	1.1
Ammonium citrate	0.06	0.1	-	-	-
Na chloride	-	1.0	-	-	-
Mg chloride	3.3	-	0.7	-	-
Ca chloride	-	-	0.4	-	-
Na sulfate	-	-	0.06	-	-
Mg sulfate	0.08	-	-	-	-
Mg hydroxide	-	-	-	2.2	2.2
Na hydroxide	-	-	-	1.1	1.1
Hydrogen peroxide	200ppm	0.16	0.006	-	-
ARP3	0.3	-	0.1	-	0.1
ARP1	-	0.3	-	0.1	0.1
Protease	0.017	0.005	0.0035	0.003	0.002
Perfume	0.18	0.09	0.09	0.2	0.2
Water and minors	Up to 100%				

**Example 21**

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**[0172]** The following liquid hard surface cleaning compositions were prepared according to the present invention :

	CA	CB	CD	CE	CF
ARP2	0.04	-	0.08	-	0.01
ARP3	-	0.3	-	0.125	0.1
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	1.0	-
LAS	0.5	0.5	0.5	-	-
C12 AS	0.5	0.5	0.5	-	-
C10AS	-	-	-	-	1.7
C12(E)S	0.5	0.5	0.5	-	-
C12,13 E6.5 nonionic	7.0	7.0	7.0	-	-
Neodol 23-6.5	-	-	-	12.0	-
Dobanol 23-3	-	-	-	-	1.5
Dobanol 91-10	-	-	-	-	1.6
C25AE1.8S	-	-	-	6.0	-
Na paraffin sulphonate	-	-	-	6.0	-
Perfume	1.0	1.0	1.0	0.5	0.2
Propanediol	-	-	-	1.5	-
Ethoxylated tetraethylene pentamine	-	-	-	1.0	-
2, Butyl octanol	-	-	-	-	0.5
Hexyl carbitol**	1.0	1.0	1.0	-	-
SCS	1.3	1.3	1.3	-	-
pH adjusted to	7-12	7-12	7-12	4	-
Miscellaneous and water	Up to 100%				

\*Na4 ethylenediamine diacetic acid

\*\*Diethylene glycol monohexyl ether

## Example 22

**[0173]** The following spray composition for cleaning of hard surfaces and removing household mildew was prepared according to the present invention :

ARP2	0.04
Amylase	0.01
Protease	0.01
Na octyl sulfate	2.0
Na dodecyl sulfate	4.0
Na hydroxide	0.8
Silicate	0.04
Butyl carbitol*	4.0
Perfume	0.35
Water/minors	up to 100%

\*Diethylene glycol monobutyl ether

Example 23

[0174] The following lavatory cleansing block compositions were prepared according to the present invention.

	CK	CL	CM
C16-18 fatty alcohol/50EO	80.0	-	-
LAS	-	-	80.0
Nonionic	-	1.0	-
Oleoamide surfactant	-	26.0	-
Partially esterified copolymer of vinylmethyl ether and maleic anhydride, viscosity 0.1-0.5	5.0	-	-
Polyethylene glycol MW 8000	-	39.0	-
Water-soluble K-polyacrylate MW 4000-8000	-	12.0	-
Water-soluble Na-copolymer of acrylamide (70%) and acrylic acid (30%) low MW	-	19.0	-
Na triphosphate	10.0	-	-
Carbonate	-	-	8.0
ARP2	0.04	-	0.01
ARP3	-	0.25	0.1
Dye	2.5	1.0	1.0
Perfume	3.0	-	7.0
KOH / HCL solution		pH 6-11	

Example 24

[0175] The following toilet bowl cleaning composition was prepared according to the present invention.

	CN	CO
C14-15 linear alcohol 7EO	2.0	10.0
Citric acid	10.0	5.0
ARP2	0.04	-
ARP3	-	0.1
DTPMP	-	1.0
Dye	2.0	1.0
Perfume	3.0	3.0
NaOH	pH 6-11	
Water and minors	Up to 100%	

**Claims**

1. A laundry and/or cleaning composition comprising a detergent ingredient and a product of reaction between an amino functional polymer comprising at least one primary amine group and a perfume component selected from ketone, aldehyde, and mixtures thereof, characterised in that said amino functional polymer has an Odour Intensity Index of less than that of a 1 % solution of methylantranilate in dipropylene glycol, and the product of reaction has a Dry Surface Odour Index of more than 5.
2. A composition according to Claim 1 wherein said amino functional polymer comprises more than one amino groups, preferably more than 10 amino groups.

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3. A composition according to Claims 1-2 wherein said amino functional polymer has a molecular weight ranging from 150 to 2.10E6; preferably from 400-50,000; more preferably from 600 to 40,000.
4. A composition according to Claims 1-3, wherein said amino functional polymer is selected from Polyvinylamine with a MW of about 300 to 2.10E6; Polyvinylamine alkoxyated with a MW of about 6K to 30K and an ethoxylation degree of 0.5; Polyvinylamine vinylalcohol with a molar ratio of 2:1; Polyvinylaminevinylformamide with a molar ratio of 1:2; Polyvinylamine vinylformamide with a molar ratio of 2:1; Triethylenetetramine; Diethylenetriamine; Tetraethylenepentamine; bis-aminopropylpiperazine; Polyamino acid of L-lysine / lauric acid in a molar ratio of 10/1; Polyamino acid of L-lysine / aminocaproic acid / adipic acid in a molar ratio of 5/5/1; Polyamino acid of L-lysine / aminocaproic acid / ethylhexanoic acid in a molar ratio of 5/3/1; Polyamino acid of polylysine-cocaprolactam; Amino substituted polyvinylalcohol with a MW ranging from 400-300,000; Polyoxyethylene bis [amine]; Polyoxyethylene bis [6-aminoethyl]; N,N'-bis-(3-aminopropyl)-1,3-propanediamine linear or branched; 1,4-bis-(3-aminopropyl) piperazine; and/or mixtures thereof.
5. A composition according to Claim 4, wherein said amino functional polymer is selected from polyvinylamines with a MW ranging from 600 to 50K; amino substituted polyvinylalcohol with a MW ranging from 400-300,000; polyoxyethylene bis [amine]; polyoxyethylene bis [6-aminoethyl]; N,N'-bis-(3-aminopropyl)-1,3-propanediamine; 1,4-bis-(3-aminopropyl) piperazine, and/or mixtures thereof.
6. A composition according to any one of Claims 1-5, wherein said product of reaction is preformed before incorporation into the laundry and cleaning composition.
7. A composition according to any one of Claims 1-6, wherein said product of reaction is present in an amount of from 0.0001% to 10%, preferably from 0.001% to 5%, and more preferably from 0.01% to 2%, by weight of the composition.
8. A composition according to Claims 1-7, wherein said perfume is a perfume aldehyde selected from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amyI cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Bucinal, lylal, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof.
9. A composition according to Claim 1-7, wherein said perfume is a perfume ketone selected from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.
10. A composition according to claims 1-7 wherein said perfume has an Odor Detection Threshold lower than 1ppm, more preferably lower than 10ppb.
11. A compositions according to Claim 10 wherein said perfume is selected from undecylenic aldehyde, undecalactone gamma, heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxy-phenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methyl-nonyl ketone, and/or mixtures thereof.
12. A method of delivering residual fragrance to a surface which comprises the steps of contacting said surface with a composition as defined in any one of Claims 1-11, and thereafter contacting the treated surface with a material so that the perfume is released.
13. A method according to Claim 12, wherein said material is water.
14. Use of a compound as defined in any one of Claim 1-11, for the manufacture of a laundry and cleaning composition for delivering residual fragrance on a surface on which it is applied.
15. Use according to Claim 14, wherein said surface is a fabric.
16. Use according to Claim 14, wherein said surface is a tile and/or ceramic.
17. A method of providing improved fabric appearance, improved protection against fabric wear and improved color care to a fabric surface, especially after multiwash cycles, which comprises the steps of contacting said surface with a product of reaction between a primary amine compound and an active component selected from ketone, aldehyde, and mixtures thereof or composition as defined in any one of Claims 1-11.





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# EUROPEAN SEARCH REPORT

Application Number  
EP 99 87 0025

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Place of search <b>THE HAGUE</b>		Date of completion of the search <b>25 October 1999</b>	Examiner <b>Loiselet-Taisne, S</b>
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons *: member of the same patent family, corresponding document</p>			

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<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons  &amp; : member of the same patent family, corresponding document</p>			

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